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Leaching kinetics of copper from waste printed circuit boards by electro-generated chlorine in HCl solution

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ABSTRACT

The leaching behavior of metals such as copper, zinc, lead and tin from waste printed circuit boards (PCBs) has been investigated using electro-generated chlorine in hydrochloric acid solution. The experiments were carried out by employing two different reactors: (a) a combined reactor facilitated with simultaneous Cl_2 generation and metal leaching, and (b) a separate metal leaching reactor connected with the anode compartment of a Cl_2 gas generator. Leaching efficiency in two reactors was compared for recycling of valuable metals from the PCBs. It was observed that the leaching rate of the metals increased with increase in current density, temperature and time in both reactors. The copper leaching rate gradually diminished when its dissolution was around 20 and 25% in the combined and separate reactor, respectively, which may be attributed to a decrease in surface area of copper with leaching time and the formation of $CuCl_{(s)}$ on the surface. The leaching efficiency of copper was found to be lower in the combined reactor than that of the separate reactor. The dissolution kinetics of copper with electro-generated chlorine followed empirical logarithmic law controlled by surface layer diffusion. The leaching mechanism of copper was further corroborated by SEM-EDS study of the residue. The activation energy for copper leaching in the combined and separate reactors was calculated to be 24.5 and 20.7 kJ/mol, respectively in the temperature range 298–323 K.

1. Introduction

There has been an increasing concern about the growing volume of waste electric and electronic equipment (WEEE) world over. It is estimated that between 20 and 50 million t of electronic waste is generated internationally each year and this will increase at a rate of 3 to 5% per annum (Heart, 2007). Printed circuit boards (PCBs) are important parts of them and contain both valuable and hazardous metals such as Au, Ag, Pd, Pt, Cu, Sn, Fe, Al, Pb, Zn, Ni, Sb, As, Be, Br, Cd, Cr, etc. (Brodersen, 1992; Goosey and Kellner, 2003). Therefore, efficient recycling is required to conserve the metallic resources and to prevent environmental pollution at the same time.

For the recycling of waste PCBs, the prevailing commercial processes in vogue follow the pyrometallurgical route utilizing a copper smelter and focuses mainly on the recovery of copper and precious metals. However, the pyrometallurgical methods have some disadvantages such as generation of large amount of slag, loss of precious metals, and difficulty in recovery of Al, Fe and other metals (Cui and Zhang, 2008). Moreover, stringent environmental regulations have stimulated further research on the recycling of waste PCBs through environmental friendly and energy-saving hydrometallurgical processes as an alternative to the pyrometallurgical routes (Cui and Zhang, 2008; Lee et al., 2007; Kaya and Sőzeri, 2009).

The hydrometallurgical methods that have been proposed to replace the pyrometallurgical methods have several drawbacks such as significant generation of liquid wastes and slow kinetics. Also, existing technologies are not available for the recovery of all valuable metals from waste PCBs. On the other hand, the leaching of metals from waste PCBs by utilizing electro-oxidation methods can reduce the amount of acids and recover valuable metals without loss. The recycling of metal components from waste PCBs by employing electro-oxidation methods has been explored using chlorine (Brandon et al., 2001, 2002; Kim et al., 2006), oxygen and HClO (Ping et al., 2009), and Cu(II) in ammonia solution (Koyama et al., 2006). Brandon et al. (2001, 2002) reported the thermodynamic prediction of metal dissolution in the chlorine/chloride solution and focused on the selective deposition of leach metals from the electronic scrap. Though, chlorine gas may be considered toxic, it has advantage of the leaching of precious metals as well as base metals of waste PCBs because of acquiring high oxidation potential (Muir, 2002).

The leaching of copper from copper powder and also from waste PCBs by electro-generated chlorine has been investigated in our laboratory (Kim et al., 2006, 2008, 2010). These studies mainly focused on the leaching mechanism and behavior of copper by

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electro-generated chlorine. It is therefore, considered necessary to develop the process in order to consume chlorine gas more safely and in an environment friendly manner to extract copper and other metals from the waste PCBs effectively while investigating the dissolution kinetics of copper.

This study examines the leaching of copper and various metals from waste PCBs, especially copper, using the electro-generated chlorine in hydrochloric acid solution by employing two different reactors: (a) a combined reactor facilitated with simultaneous Cl_2 generation and metal leaching which can circulate and reuse chloride ion without additional supplementation, and (b) a separate metal leaching reactor connected with the anode compartment of a Cl_2 gas generator which can attain the optimum chlorine consumption. While optimizing the process parameters such as current density, leaching time and temperature on the dissolution of metals the kinetics of copper leaching was investigated and results are discussed in this paper.

2. Experimental

2.1. Materials

The nonmagnetic portion of the waste PCBs of size 1.4–3.0 mm, free from the naked metallic component, was used as the sample for the leaching tests. Nonmagnetic metal component of waste PCBs was obtained by crushing and magnetic separation. The composition of the sample listed in Table 1 shows copper (18–20%) as the major metal. All chemicals used were analytical grade reagents.

2.2. Methods

The leaching test by electro-generated chlorine was conducted using electrolytic cells. The cell was made of acrylic and was divided into two compartments by an anion exchange membrane (Neosepta AMX, Tokuyama Co.). Two cathodes and anodes were used in these experiments. Both electrodes were made of high purity graphite rods (20 cm (l) × 0.8 cm (d)) with an effective area — 14.0 cm^2/electrode in solution. A constant current was supplied in order to electro-generate chlorine gas at the anode using a programmable DC power supply (IPS-30B10, INTERACT Co., Ltd.). The operating potential of the electrolytic cells was in the range 3.2 to 4.5 V with the current efficiency of chlorine generation of 98 ± 3% (Kim et al., 2008).

2.3. Experimental procedure

Fig. 1 shows the schematic diagram of the reactors. The combined reactor (Fig. 1(a)) consisted of a single electrolytic cell in which the sample of waste PCBs was charged directly to facilitate the simultaneous chlorine generation and metal leaching (Kim et al., 2008, 2010). A rectangular vessel of dimension — 20 cm × 10 cm × 10 cm was used as a combined reactor while dividing it into two compartments by a membrane. A provision was made for heating the reactor externally in a thermostatically controlled water bath and measuring the solution temperature through a thermocouple. In a typical run, 600 mL of the acid solutions of the same concentrations (1.0–4.0 mol/L HCl) were

Table 1
Composition of PCB sample for electrogenerated chlorine leaching.

Elements	Wt.%
Cu	19 ± 1.0
Zn	0.26
Al	1.10
Pb	0.51
Sn	0.95

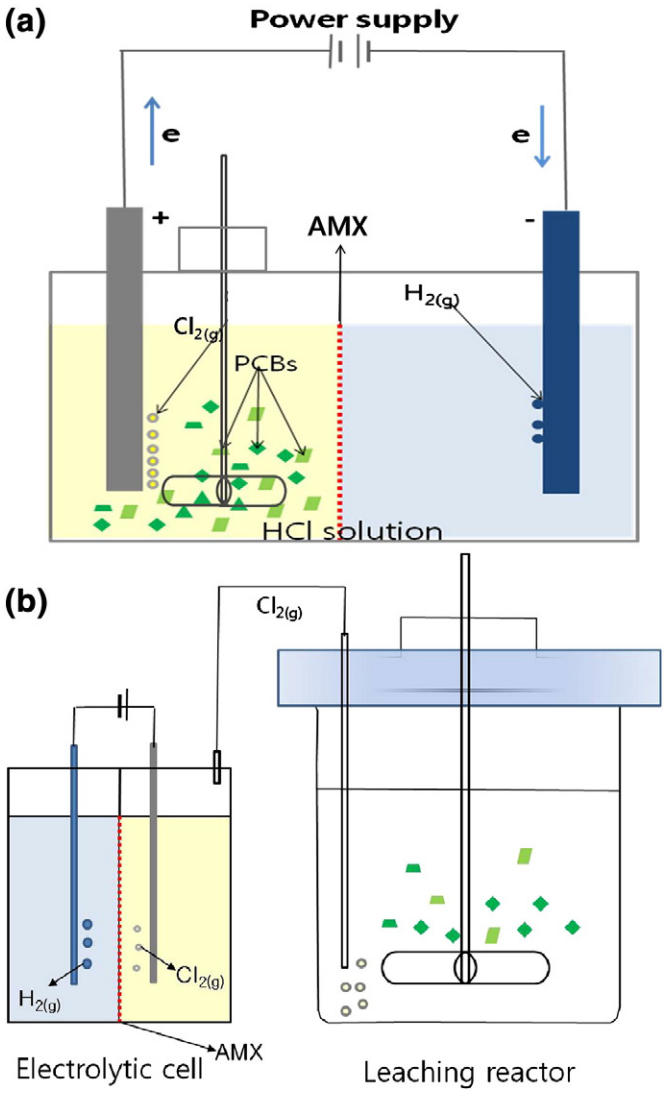

Fig. 1. Schematic diagram of the apparatus: (a) combined reactor and (b) separate reactor.

poured into the anode chamber (reactor) and the cathodic compartment heated to a desired temperature. During the leaching, the concentration of free Cl^- was partially compensated by the Cl^- migration through the anion exchange membrane from cathodic compartment. This was followed by the addition of 10 g of the PCBs sample into the reactor. The solution in the anode compartment was agitated by a PTFE-coated stainless steel impeller at 400 rpm in conjunction with the electro-generation of chlorine for the leaching test.

On the other hand, the separate reactor (Fig. 1(b)) consisted of an electrolytic cell for chlorine generation and a separate vessel (reactor) for the metal leaching. The electrolytic cell of acrylic of size 18 cm × 9 cm × 12.5 cm was divided into two compartments with a membrane. The thermocouple was inserted in the leaching reactor through the side opening to measure the temperature. In the anode and cathode compartments of the electrolytic cell 200 mL of 4.0 mol/L and 6.0 mol/L hydrochloric acid solution was poured, respectively and then the anode compartment was saturated with chlorine by supplying constant current across the electrodes before starting the leaching. After saturation of anode compartment of the cell, 600 mL of hydrochloric acid (1.0–4.0 mol/L) was poured into the leaching reactor and the solution was heated to the desired temperature by electrically controlled heating element. A 10 g sample was then added for the experiment. The electro-generated chlorine gas from the electrolytic cell (Fig. 1(b)) was passed to the leaching reactor through

a tube. The solution in the leaching reactor was also agitated by a PTFE-coated steel impeller at a speed of 400 rpm.

2.4. Analysis

The samples at the predetermined time periods were taken out from the reactors and were analyzed by atomic absorption spectrometer (AAnalyst 400, PerkinElmer Inc.). The oxidation and reduction potential (ORP, mV vs. Ag/AgCl) in the leach solution was measured and total concentration of oxidants (residual $Cl_2(aq) + Cu(II)$) was analyzed by titration using the iodide-thiosulfate method (Kim et al., 2010). The leach residue was characterized for its chemical composition and surface morphology with a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM/EDS, JSM-6400, Jeol Ltd.).

3. Results and discussion

Chlorine generation from hydrochloric acid solution can be represented (Pilone and Kelsall, 2006) by the following reaction:

$$\textbf{Anode: } 2Cl^- \rightarrow Cl_2(\text{electrode surface}) + 2e^- \qquad E^0 = 1.35V_{SHE} \quad (1)$$

The generated chlorine gas by Eq. (1) dissolves in water as follows:

$$Cl_{2(g)} \leftrightarrow Cl_{2(aq)} \quad (2)$$

$$Cl_{2(aq)} + H_2O \leftrightarrow HCl + HOCl \quad (3)$$

$$Cl_{2(aq)} + Cl^- \leftrightarrow Cl_3^- \quad (4)$$

The distribution of these species depends on the concentration of HCl, pH and temperature (Alkan et al., 2005; Majima et al., 1990).

3.1. Copper metal leaching in different reactors

The dissolution reactions of copper in acidic chloride solution can be represented as (Muir, 2002; Kim et al., 2008; Pilone and Kelsall, 2006):

$$\textbf{Leach: } Cu + Cl_{2(aq)} \rightarrow Cu^{2+} + 2Cl^- \quad (5)$$

$$Cu + Cl_3^- \rightarrow Cu^{2+} + 3Cl^- \quad (6)$$

$$Cu^{2+} + Cu \rightarrow 2Cu^+ \quad (7)$$

As a result, one mole of chlorine can oxidize two moles of copper to cuprous state by obtaining two electrons. However, when the dissolution rate of chlorine is faster than leaching rate of copper with cupric ions (Eq. (7)), cuprous ions are oxidized with chlorine as follows:

$$\textbf{Oxidation: } 2Cu^+ + Cl_{2(aq)} \rightarrow 2Cu^{2+} + 2Cl^- \quad (8)$$

Also, in the combined reactor, when the cuprous ion is generated in the leach solution by Eq. (7), cuprous oxidation at anode may also be anticipated (Kim et al., 2008) as:

$$\textbf{Anode: } Cu^+ \rightarrow Cu^{2+} + e^- \qquad E^0 = 0.15V_{SHE} \quad (9)$$

Fig. 2(a) shows the results of copper (%) leached and ORP values acquired with time. The experiments were initially conducted using copper granules (purity, 99.9%; −0.85/+0.6 mm) in different reactors. The leaching rate of copper was noted to be the same up to 30 min and beyond that the leaching rate retarded in the combined reactor than that of separate reactor (Fig. 2(a)). This may be due to the change of reaction at anode from Eq. (1) to the mixing of Eqs. (1) and (9). In the combined reactor all the reactions corresponding to both process steps i.e. electro-oxidation (Eqs. (1) and (9)) and leaching (Eqs. (5)–(7)) are involved in the same compartment, it is therefore, likely that the two processes may affect each other during the leaching. The cuprous ions produced from copper dissolution by Eq. (7) has decreased the amount of chlorine generated at anode by Eq. (9), because of lower oxidation potential of cuprous ions than that of chloride ions causing the preferential generation of cupric ions. When the concentration of cuprous ions available at the anode is high enough to consume the applied current, the anode reaction changes from the mixed reaction of Cl_2 generation (Eq. (1)) and cuprous oxidation (Eq. (9)) to the only cuprous oxidation (Eq. (9)) reaction (Kim et al., 2008). This seems to have resulted in the lower leaching efficiency in the combined reactor than that of the separate reactor. Almost steady ORP values observed for the leaching in combined reactor after initial rise signify the prevailing oxidizing conditions and cupric ions in the solution. The drop in ORP in separate reactor is caused by the consumption of chlorine and increased concentration of cuprous ions in leach solution through the leaching reactions (5), (6), and (7). Fig. 2(b) shows concentration of total Cu, cuprous and cupric

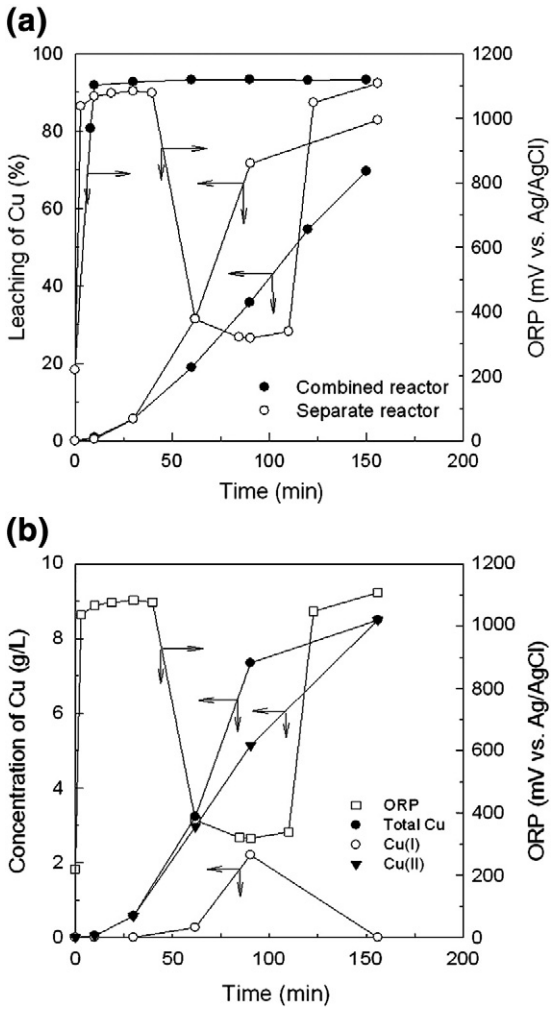

Fig. 2. (a) Leached copper (%) and ORP (mV vs. Ag/AgCl) with time using different reactors and (b) concentration of Cu, Cu(I), and Cu(II) with time in separate reactor (Temperature, 298 K; HCl concentration, 2.0 mol/L; current density, 714 A/m^2; agitation speed, 400 rpm, Cu granule, −0.85/+0.6 mm, 99.9%).

ions with time during electro-generated chlorine leaching in the separate reactor. The ORP drop caused by the generation of cuprous ions in the solution resulted in increased copper leaching efficiency simultaneously. The increase in ORP after 120 min in separate reactor (Fig. 2.(b)) may be accounted for increasing concentration of residual chlorine with a decrease in copper leaching due to the reduced surface area of the substrate.

3.2. Copper leaching from waste PCBs

3.2.1. Effect of leaching time

The leaching of copper from the waste PCBs was studied with time in different reactors and results are plotted in Fig. 3. Based on the preliminary experiments the stirring speed was fixed at 400 rpm to eliminate the effect of liquid film diffusion on the leaching efficiency.

Initially, the leaching rate of copper was almost same with increase in leaching time, though the extent of leaching was a little higher in separate reactor than that of combined reactor. The ORP drop after 250 min (Fig. 3) in the separate reactor indicated that no significant Cl_2 was present in the solution. This indicated that the $Cl_{2(g)}$ injected seems totally absorbed in the gas–liquid interface by the Cu(I) aqueous complexes to form Cu(II) complexes. Thus, under these conditions the unique leaching agent in the solid-interface seems to be the Cu(II) (as complexes). In comparison to the rate of copper metal solubilization (Fig. 2(a)), the leaching rate of copper from PCBs sample was slower. Also, it gradually diminished when the leaching time approached to 350 min, which may be due to decreasing surface area of copper with leaching time and formation of $CuCl_{(s)}$ on the surface as discussed later. The formation of cuprous chloride may be reduced by decreasing the generation of cuprous ions or increasing the solubility of CuCl. Therefore, the effect of current density, temperature and concentration of hydrochloric acid on copper leaching from the waste PCBs was investigated.

3.2.2. Effect of current density

Fig. 4(a) shows the effect of applied current density on the electro-generated chlorine leaching of copper with time using different reactors. As can be seen, the leaching of copper increased with increase in the current density. In particular, with increase in current density from 286 A/m^2 (I = 0.8 A) to 714 A/m^2 (I = 2 A), the copper leaching achieved was almost constant at higher duration of experiments. The leaching rate, however, gradually diminished when the copper dissolution was around 20% (Fig. 4(a)) and 25% (Fig. 4(b)) in the combined reactor and separate reactor, respectively.

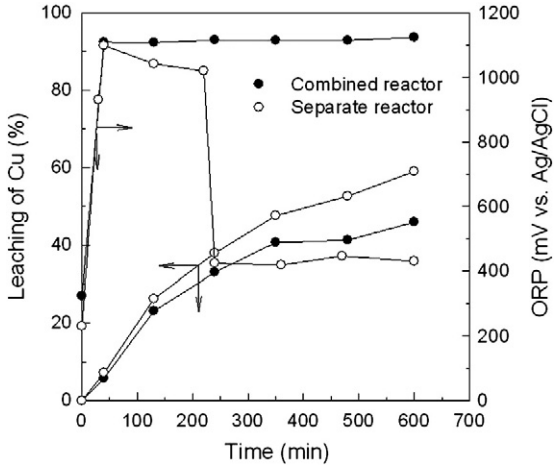

Fig. 3. Leached copper (%) and ORP (mV vs. Ag/AgCl) with time using different reactors from waste PCBs (Temperature, 298 K; HCl concentration, 2.0 mol/L; current density, 286 A/m^2; agitation speed, 400 rpm; S/L ratio, 17 g/L).

3.2.3. Effect of leaching temperature

Fig. 5 shows the pattern of copper leaching (%) from the PCBs sample in solution, as a function of temperature at a fixed HCl concentration (2.0 mol/L) in the bath, and the applied current density of 714 A/m^2. As the temperature increased, the percentage leaching of copper also increased. The maximum copper leaching was 71% at 323 K and 240 min in the separate reactor. Although, the solubility of aqueous chlorine is reported to decrease with increase in temperature (Pilone and Kelsall, 2006), the increase in copper leaching at higher temperature may be attributed to the enhanced diffusivity of chlorine (Marsden and House, 2006) and substantial increase in the leaching rate of $CuCl_s$ in HCl media (Winand, 1991).

3.2.4. Effect of chloride concentration

The percentage leaching of copper as a function of hydrochloric acid concentration in the range 1.0–4.0 mol/L at 298 K and 714 A/m^2 current density is given in Fig. 6. Raising the concentration of hydrochloric acid had no effect on the extent of copper leaching till 90 min. Copper leaching then increased significantly when the acid concentration was increased from 1.0 to 3.0 mol/L HCl with time. The increase in copper leaching after 90 min may be due to the increased solubility of CuCl in hydrochloric acid at higher chloride concentration. However, the increase in leaching rate was not appreciable with increase in HCl concentration from 3.0 to 4.0 mol/L.

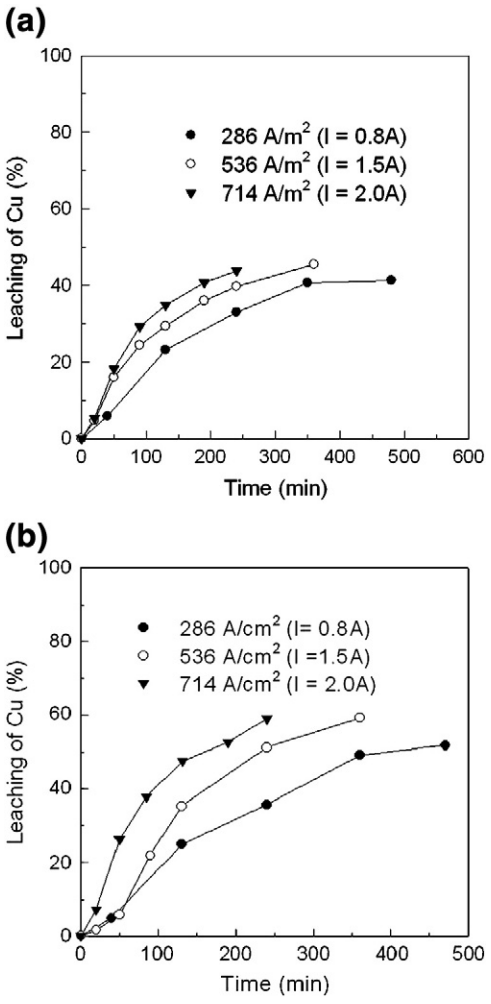

Fig. 4. Leaching of copper from waste PCBs with time at varying current density in (a) combined reactor, and (b) separate reactor (S/L ratio, 17 g/L; temperature, 298 K; HCl concentration, 2.0 mol/L; agitation speed, 400 rpm).

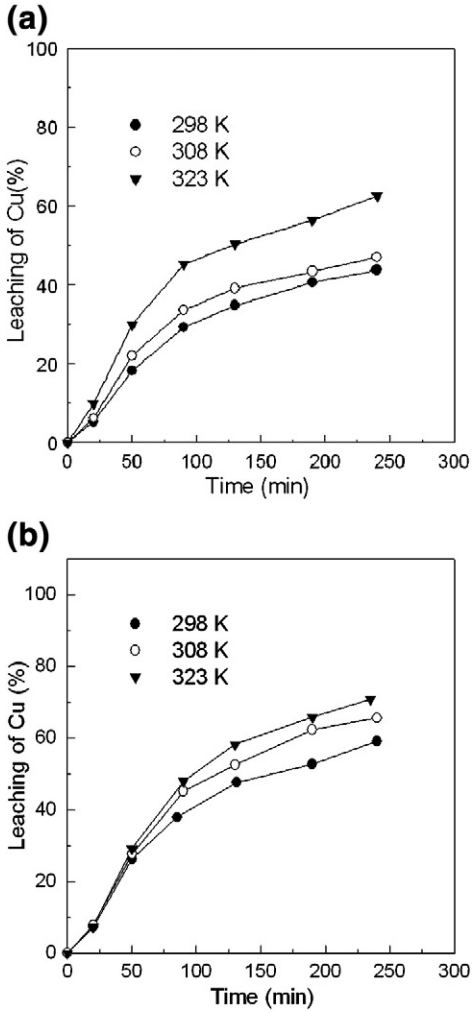

Fig. 5. Effect of temperature on copper (%) with time in (a) combined reactor and (b) separate reactor (S/L ratio, 17 g/L; HCl concentration, 2 mol/L; agitation speed, 400 rpm; current density, 714 A/m^2).

3.2.5. Analysis of leach residue

The leach residue obtained from the electro-generated chlorine leaching of waste PCBs sample in the separate reactor with 2.0 mol/L HCl at a current density of 714 A/m^2 and 298 K temperature was examined for surface morphology and elemental distribution by SEM/EDS. The images are shown in Fig. 7(a)–(e). In the initial stage, the sample leached in 20 min (Fig. 7(a1)) shows the corroded surface of copper on both upper and lower sides which is lying between the insulating layers. The EDS (Fig. 7(a2)) corresponding to this sample indicates the presence of copper metal mainly along with small amount of aluminum. A look at the SEM image (Fig. 7(b1)) of the leach residue in 50 min however, shows that the copper surface is uniformly covered by CuCl layer formed as the reaction product which is clearly reflected by EDS presented in Fig. 7(b2). Thus, the formation of cuprous chloride on the substrate which is contained between the insulating materials as shown in Fig. 7(b1), implies the hindered diffusion of chlorine to the copper surface. The SEM picture of the cross section of the residue in 50 min leaching by removing the upper insulating layer can be seen from Fig. 7(c) and a view of the marked portion in Fig. 7(d). These images further show the corroded surface because of the metal leaching from the substrate adjacent to the insulating layer; the dissolution of copper being ~25% under this condition (Fig. 2(b)). The cross section of the leach residue after 240 min was also examined by SEM/EDS and mapping of different elements is shown in Fig. 7(e). These pictures clearly reflect the formation of solid cuprous chloride which uniformly covers the copper surface as a result of chlorine leaching. The presence of insulating layer around the edges is also apparent from Fig. 7(e).

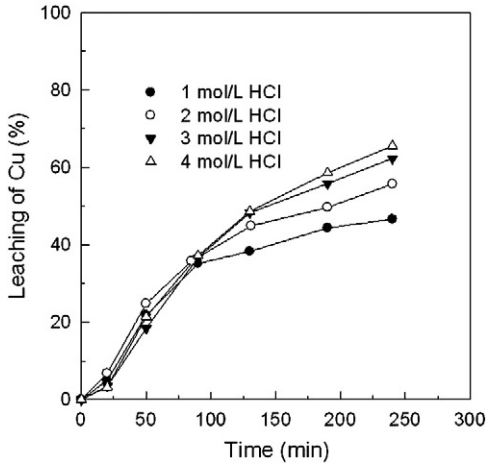

Fig. 6. Effect of HCl concentration on copper leaching with time in separate reactor (S/L ratio, 17 g/L; temperature, 298 K; agitation speed, 400 rpm; current density, 714 A/m^2).

3.3. Leaching kinetics analysis

The kinetics of copper leaching from waste PCBs were also studied using the two reactors. Due to the complex geometric nature of the sample and the change of the concentration of the oxidant (i.e. dissolved chlorine and Cu(II)), an empirical model comprising of logarithmic law for kinetic study (Levenspiel, 1999) was introduced as shown in Eq. (10).

$$(-\ln(1-\alpha))^2 = k\,t \tag{10}$$

Where, α is the fraction of Cu reacted in time t and k is the apparent rate constant.

The mode of reaction for copper dissolution was studied by calculating the values of rate constants (k) and the correlation coefficients in both reactors. The plots of $(-\ln(1-\alpha))^2$ vs t at different temperatures as depicted in Fig. 8(a, b) show a good fit. Attempts to fit the leaching kinetic data to the parabolic law ($\alpha^2 = k\,t$) were not successful.

The Arrhenius plot is shown in Fig. 9 by considering the apparent rate constant values (k) obtained from Fig. 8 under the experimental leaching conditions of Fig. 5. The values of activation energy were calculated to be 24.5 kJ/mol and 20.7 kJ/mol for the combined reactor and separate reactor, respectively in the temperature range 298–323 K. This indicated that the reaction was controlled by mass transfer. Herreros et al. (1999) reported the activation energy value for copper metal leaching with chlorine as 17.4 kJ/mol, which is very similar to the value acquired for the leaching of PCBs in the separate reactor. They reported the film diffusion control by chlorine as the mode of leaching. The difference in mode of leaching in the present case is possibly due to the sample morphology. Unlike the copper metal used by Herreros et al. (1999) for chlorine leaching, copper in the PCBs is contained between the insulating materials making the diffusion of the reactant and the products such as chlorine and cuprous ions difficult. In this condition copper leached out as cupric ions initially by Eqs. (5) and (6) is converted to the cuprous ions by additional cupric leaching by Eq. (7). Since the solubility of cuprous chloride is low, it forms a precipitated layer on the copper surface which inhibits the leaching. A look at Figs. 4–6 further showed that the leaching of copper was controlled by chlorine diffusion till around 20% (combined reactor) −25% (separate reactor) leaching and then the

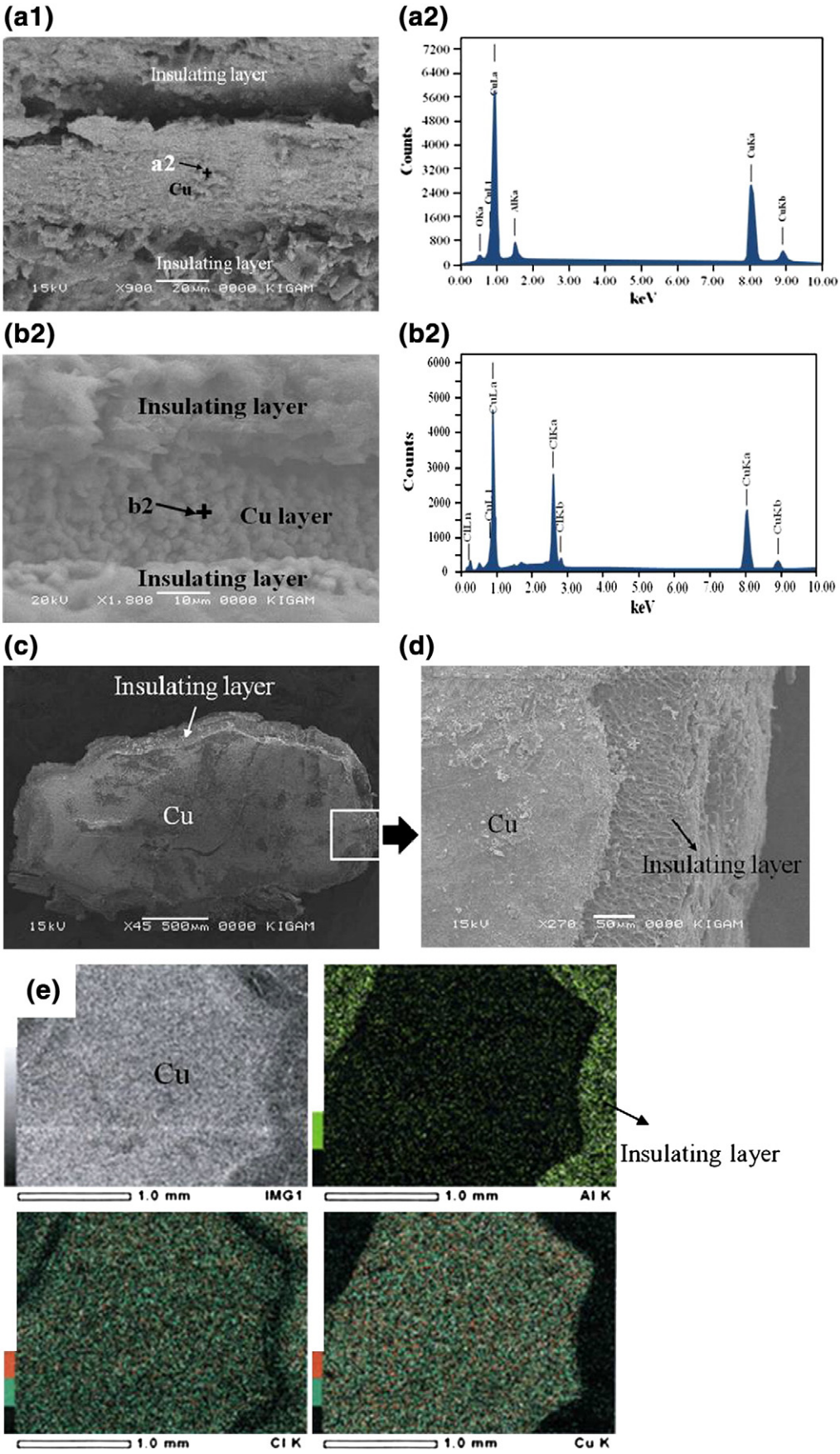

Fig. 7. SEM/EDS of the leached samples; (a1) SEM image after 20 min, (a2) EDS of (al), (b1) SEM image after 50 min, (b2) EDS of (b1), (c) SEM image after 50 min (cross section) and (d) the marked area of (c), (e) EDS mapping after 240 min (S/L ratio, 17 g/L; temperature, 298 K; agitation speed, 400 rpm; current density, 714 A/m^2).

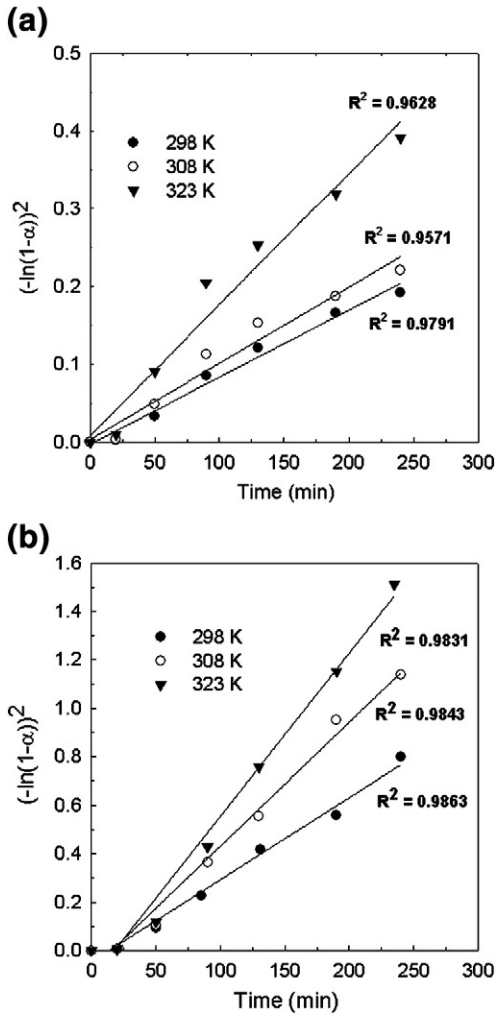

Fig. 8. Plot of $(-\ln(1-\alpha))^2$ vs. t at different temperature in (a) the combined reactor and (b) the separate reactor.

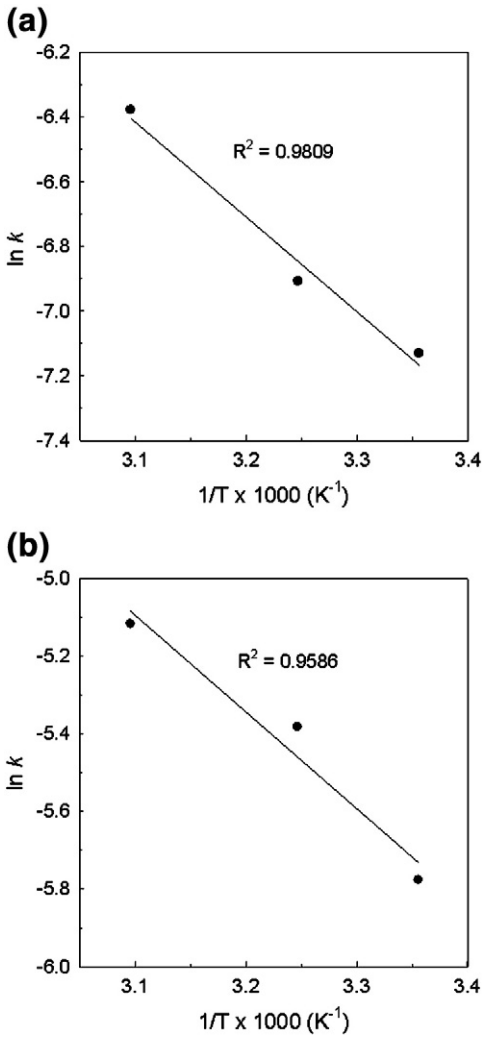

Fig. 9. Arrhenius plot for leaching in (a) the combined reactor and (b) the separate reactor.

dissolution was retarded. This may be attributed to the formation of cuprous chloride on the copper surface as can be seen from the SEM/EDS study (Fig. 7(a–e)) of the sample after 50 min of leaching. The diffusion of the lixiviant, chlorine through the porous product layer i.e. cuprous chloride formed on the substrate may be considered as the rate-limiting step for the leaching of copper from the waste PCBs. It may also be mentioned that in the initial stage of copper leaching (up to 25%), the predominant mechanism could be the film diffusion control by chlorine and not by the ash diffusion control, as reported by Herreros et al. (1999).

In the combined reactor, the activation energy was slightly higher than that of the separate reactor. This may be due to the involvement of cupric leaching with the change of anodic reaction from chlorine generation to the mixing of chlorine and cuprous ion oxidation by Eqs. (1) and (9) during copper leaching. The activation energy value acquired (24.5 kJ/mol) in the present case for the leaching of PCBs in combined reactor is near to the value of 28 kJ/mol as reported by Herreros et al. (2005) for the cupric leaching of copper.

The results on the effect of current density on the copper leaching in separate reactor (Fig. 4(b)) were also applied to this kinetic model at 298 K. The plots between $(-\ln(1-\alpha))^2$ vs t for the applied current density show good fit to the logarithmic rate law controlled by the surface layer diffusion of the lixiviants (Fig. 10) with high correlation coefficients (>0.95).

Table 2 shows the values of k_{app} (apparent rate constant) at varying current density to generate chlorine. The k_{app} values were found to be in the range 1.2×10^{-3} to 3.4×10^{-3}/min. Also, the relationship between the k_{app} and the current density was found to be linear with a correlation coefficient of 0.99 as shown in Fig. 11. It may thus be reasonable to assume that equilibrium was established

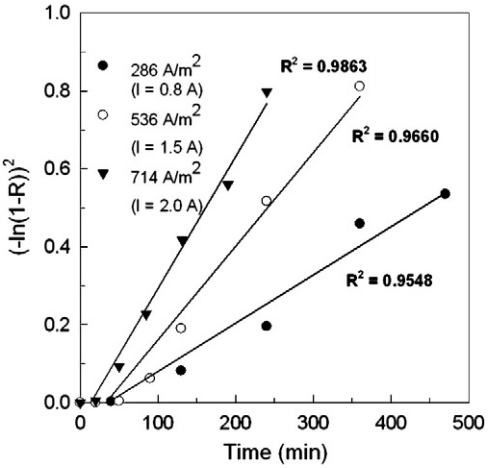

Fig. 10. Plot of $(-\ln(1-\alpha))^2$ vs. t at varying applied current density in the separate reactor.

Table 2
Apparent rate constant, k_{app} with current density.

Current density (A/m^2)	k_{app} ($\times 10^{-3}\,min^{-1}$)
290	1.2
540	2.4
718	3.4

between the chlorine electrochemically generated by the applied current and the dissolved chlorine species taking part in the leaching of copper under the experimental conditions mentioned in Fig. 4(b). The higher the current density applied for chlorine generation, the higher was the rate of copper leaching from the waste PCBs while still following the surface/ash layer diffusion mechanism.

Fig. 12(a) shows the concentration of chlorine with time at 298 K in the separate reactor when no metal was present in the leaching vessel. Chlorine concentration was found to vary linearly with reaction/dissolution time and increased with increase in current density in the range 178–714 A/m^2 below 3 g/L of chlorine dissolved in the hydrochloric acid solution. As can be seen from Fig. 12(b) the dissolution rate of chlorine in the hydrochloric acid solution was proportional to the applied current for electro-generation of chlorine. From these results, it may be concluded that the copper leaching rate (Fig. 11) is proportional to the dissolution rate of chlorine in the separate reactor and the current density applied in the electrolytic cell.

3.4. Leaching of different metals from the waste PCBs in the separate reactor

The subsequent experiments were carried out in the separate reactor to examine the leaching efficiency of different metals of the waste PCBs. The results of leaching of other metals such as zinc, tin and lead in addition to copper in 240 min with time are presented in Fig. 13. As can be seen from Fig. 13(a), the leaching (%) of all metals increased with increase in current density. The increase in leaching of other metals viz. zinc, lead, and tin, apart from copper in 240 min was also observed (Fig. 13(b)) with increase in temperature. At 298 K, the leaching of metals followed the order Zn>Sn>Cu>Pb. From these results it may be seen that the leaching of lead increased significantly when temperature was raised to 308 K. At this temperature, the leaching of zinc and tin was also high. Copper leaching increased gradually from 59% to 71% with increase in temperature from 298 K to 323 K. At 323 K, zinc, tin, lead and copper were leached (Fig. 13(b)) to the extent of 98, 96, 96, and 71% from the waste PCBs, respectively.

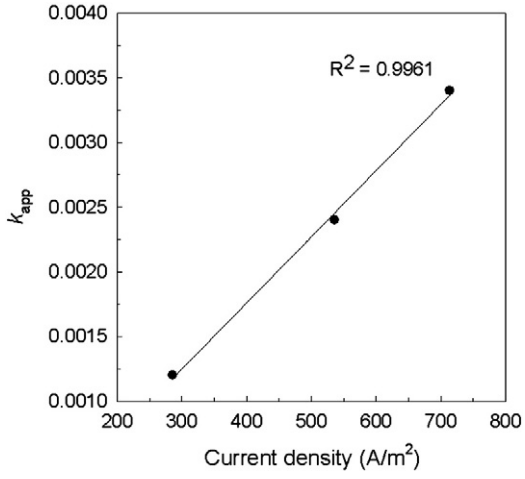

Fig. 11. Plot of k_{app} vs. current density.

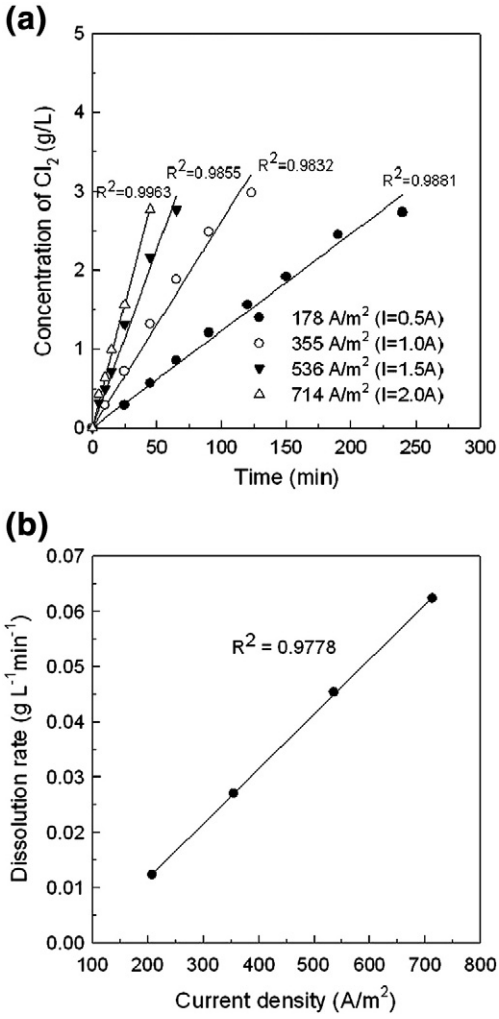

Fig. 12. (a) concentration of Cl_2 vs. time and (b) dissolution rate of chlorine vs. current density in the separate reactor (Temperature, 298 K; HCl concentration, 2.0 mol/L; agitation speed, 400 rpm).

4. Conclusions

In the present work, leaching of copper and other base metals such as lead, tin and zinc contained in the waste PCBs was investigated by electro-generated chlorine in the combined reactor and the separate reactor. Unlike previous studies for examining the leaching behavior of copper from the waste PCBs by chlorine, the kinetics of copper dissolution and effective leaching of different metals are emphasized in this investigation. In both reactors, the leaching rate of the metals from the waste PCBs increased with increase in current and temperature. However, copper leaching rate gradually diminished when the leaching was around 20% and 25% in the combined and the separate reactors, respectively, which may be due to the decrease in surface area of copper with leaching time and the formation of $CuCl_{(s)}$ on the copper surface as identified by SEM/EDS study of the leach residue. The generation of cuprous ions in combined reactor decreased the leaching efficiency due to the change of electrode reactions. In the separate reactor, leaching up to 71% copper along with 98% Zn, 96% Sn and 96% Pb was achieved using 2.0 mol/L HCl solution at a current density of 714 A/m^2, 323 K temperature and 400 rpm in 240 min. Higher rates of copper leaching were obtained with 3.0 mol/L HCl which dissolves CuCl more readily.

The copper dissolution using electro-generated chlorine was observed to follow the empirical logarithmic rate law with surface layer diffusion. The activation energy values for copper leaching

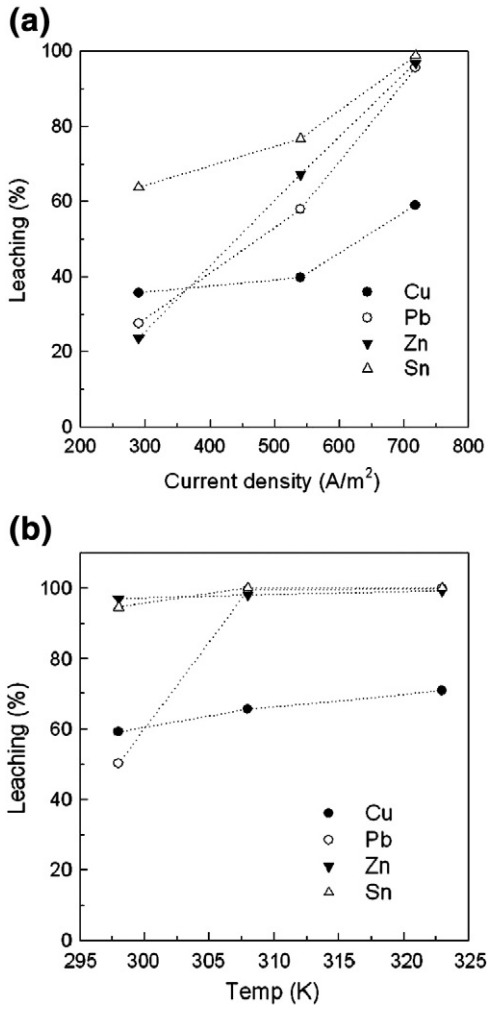

Fig. 13. Leaching of metals vs. (a) current density, and (b) temperature in the separate reactor (S/L ratio, 17 g/L; leaching time, 240 min; agitation speed, 400 rpm; HCl concentration, 2.0 mol/L).

calculated from the kinetic study were found to be 24.5 kJ/mol and 20.7 kJ/mol in the combined reactor and the separate reactor, respectively in the temperature range 298 − 323 K. Diffusion of the lixiviants through the porous product layer comprising of $CuCl_{(s)}$ being the rate controlling step for copper leaching which was corroborated by SEM-EDS study of the leach residue.

The process by electro-generated chlorine leaching can be applicable to recover precious and refractory metals by treating the wastes/scraps such as spent catalysts, e-wastes etc. Also, in order to enhance the leaching efficiency of copper with chlorine, a study of the leaching of the $CuCl_s$ previously generated on the metallic copper in HCl would be interesting and may be considered in future.

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